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Truncated diatomic orbitals for homonuclear and heteronuclear one-electron-active diatomic systems: $H_2{}^+$, HeH^{2+}, and $Li_2{}^+$

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Truncated diatomic orbitals (TDO) that we define in retaining only one term in the expansions of diatomic orbitals (DO) which are exact Born-Oppenheimer solutions of the one-electron two-center problem are proposed as basis functions for describing electronic molecular states of diatomic systems. Test calculations are performed and compared to the exact values for the electronic energy as well as for values of the wave function for some states of $H_2{}^+$ and HeH^{2+} in order to check the efficiency of the TDO's as a basis set. TDO's are then used as basis functions to describe 38 electronic states of $Li_2{}^+$ in the framework of a model-potential method, in the range $2 \le R \le 20$ a.u.

I. INTRODUCTION

During the past ten years much work has been done for the determination, in the framework of pseudopotential and model-potential methods, of accurate potential-energy curves for molecular states of diatomic systems with one active electron such as diatomic alkali-metal ions.[1–5] The corresponding wave functions, generally expanded on the basis of atomic functions, are used in subsequent configuration interaction calculations[6–8] as well as in explicitly correlated wave-function methods[9] for studies of the corresponding two-active-electron systems such as alkali-metal dimers. At this stage, the number of constituent basis functions for these one-active-electron two-center wave functions becomes an important parameter to be considered.

In fact, exact Born-Oppenheimer solutions (called diatomic orbitals) for the simplest one-electron diatomic systems (i.e., two fixed nuclei of charge Z_A and Z_B, respectively, separated by a distance R and one electron) are obtainable on semianalytical forms[10–25] with as high an accuracy as desired and because of their intrinsic diatomic feature they should constitute interesting basis functions for the approximate treatment of one-active-electron diatomic systems in the framework of model-potential methods. In the present paper we propose to use truncated diatomic orbitals (TDO's) instead of the full expansions of the diatomic orbitals (DO's), as basis functions for one-electron diatomic problems. The TDO's are defined as component parts of the DO's and are much more tractable than diatomic orbitals in usual diatomic calculations.

After having defined TDO's in Sec. II, we used them in test calculations for the energies as well as for the numerical values of the wave functions of some molecular states of $H_2{}^+$ and HeH^{2+} in Sec. III. After a recall of the $Li_2{}^+$ problem in the framework of model potential in Sec. IV, we present and discuss the results obtained on the basis of TDO's for nine Σ_g states, nine Σ_u states, five Π_g states, five Π_u states, five Δ_g states, and five Δ_u states of $Li_2{}^+$ in the range $2 \le R \le 20$ a.u.

II. DEFINITION OF TRUNCATED DIATOMIC ORBITALS (TDO)

We construct truncated diatomic orbitals from diatomic orbitals defined as eigenfunctions in prolate-spheroidal coordinates of the Schrödinger equation for the movement of one electron in the field of two fixed nuclei of charge Z_A and Z_B, respectively, separated by a distance R. This problem is an exactly soluble one and diatomic orbitals can be obtained on a semianalytical form with as high an accuracy as desired. Among the various determination procedures for DO's based on semianalytical representation of the wave function that have appeared in the literature,[10–25] one of them was proposed by us some ten years ago.[25] Briefly stated, it may be described as follows.

The following separated form, in prolate-spheroidal coordinates ($1 \le \lambda \le \infty$, $-1 \le \mu \le +1$, $0 \le \phi \le 2\pi$), is assumed for diatomic orbitals

$$\Phi(\lambda,\mu,\phi)=M(\mu,\phi)\Lambda(\lambda) , \tag{1}$$

where

$$M(\mu,\phi)=\sum_{k=m}^{K} f_k^m Y_k^m(\mu,\phi) , \tag{2}$$

$Y_k^m(\mu,\phi)$ are spherical harmonics,

$$\Lambda(\lambda)=e^{-p(\lambda-1)}[2p(\lambda-1)]^{m/2}\sum_{j=0}^{J} C_j \mathscr{L}_j^m(2p(\lambda-1)) . \tag{3}$$

$\mathscr{L}_j^m(2p(\lambda-1))$ are normalized Laguerre polynomials.

The one-electron two-center Schrödinger equation is then separated in two-coupled matricial equations. The eigenenergies $E=-2p^2/R^2$ are obtained from the simultaneous resolution of that pair of matricial equations which is achieved by a Newton-Raphson procedure. The

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expansion coefficients f_m^k and C_j are obtained as the eigenvector components of these two matrices, respectively,

$$\sum_{k=m}^{K} (f_k^m)^2=1,\quad \sum_{j=0}^{J} C_j^2=1\ .$$

It should be noted that diatomic orbitals are named by the triplet set of quantum numbers $\{n,l,m\}$ in the united atom labeling of states.

The mathematical form for the TDO's is deduced from the expressions (2) and (3) for the DO's by means of the following arbitrary choices

$$f_l^m=1,\quad f_k^m=0\ \ \forall\ k\neq l\ ,$$

$$C_{n-l-1}=1,\quad C_j=0\ \ \forall\ j\neq n-l-1\ .$$

Then, any truncated diatomic orbital ψ_{nlm} can be written

$$\psi_{nlm}(\lambda,\mu,\phi)=Y_l^m(\mu,\phi)e^{-p(\lambda-1)}[2p(\lambda-1)]^{m/2} \times\mathscr{L}_{n-l-1}^{m}(2p(\lambda-1))\ . \qquad (4)$$

In fact our arbitrary definition of TDO's is supported in some ways by the observations made upon the numerical values of the coefficients f_k^m and C_j for the DO's $\{n,l,m\}$: $n\in\{1,2,3\}$, $l\in\{0,1,2\}$, $m\in\{0,1,2\}$ of $H_2{}^+$ and of HeH^{2+} for $0.2\leq R\leq 10$ a.u. The coefficient C_{n-l-1} is often the largest and is always an important coefficient in the expansion of the function Λ [Eq. (3)]. Similar conclusions are available for the relative importance of the coefficient f_l^m in the expansion of the function M [Eq. (12)].

The parameter p involved in the formula defining the TDO's ψ_{nlm} [Eq. (4)] is determined from the general procedure applied in the particular case where the two matrices involved are reduced to one element. p is then a positive root of the following fourth degree polynomial:

$$\begin{aligned}
&-8\left[\frac{l^2+l+m^2-1}{(2l+3)(2l-1)}\right]p^4-2(2n-2l+m-1)\left[\frac{17l^2+17l+m^2-13)}{(2l+3)(2l-1)}\right]p^3\\
&\quad-2\left\{(2n-2l+m-1)^2+2(2n-2l+m-1)\left[n-l+\frac{m}{2}\right]-2[R(Z_A+Z_B)+n-(l+1)^2]-m(m+1)\right\}p^2\\
&\quad+(2n-2l+m-1)\left[3R(Z_A+Z_B)-(2n-2l+m-1)\left[n-l+\frac{m}{2}\right]+n-(l+1)^2+\frac{m}{2}\left[\frac{m}{2}+1\right]\right]p\\
&\quad+(2n-2l+m-1)^2\frac{R(Z_A+Z_B)}{2}=0\ . \qquad (5)
\end{aligned}$$

For a given TDO ψ_{nlm}, the values of p may be easily obtained from the Newton method on the whole range of R starting from a small value R_0. The process is initialized by using the value of p deduced from the united-atom approximation, i.e., $p=R(Z_A+Z_B)/2n$ as the starting value for $R=R_0$. The process is then continued for increasing values of R, using the value of p corresponding to R_{i-1} as a starting value for R_i. It is rapidly convergent.

III. TDO'S AS BASIS FUNCTIONS FOR SOME TEST CALCULATIONS FOR $H_2{}^+$ AND HeH^{2+}

In order to use the TDO's ψ_{nlm} as basis functions for the determination of the energy of one-electron diatomic systems, one has to evaluate as usual the energy matrix elements

$$H_{ij}=\langle\psi_i\,|\,H\,|\,\psi_j\rangle\ ,$$

where

$$\psi_k=\psi_{n_k l_k m_k}(\lambda,\mu,\phi)$$

and

$$H=-\tfrac{1}{2}\Delta-\frac{Z_A}{r_A}-\frac{Z_B}{r_B}\ ,$$

as well as the overlap matrix elements

$$S_{ij}=\langle\psi_i\psi_j\rangle\ .$$

This can be achieved without difficulty.

A. $H_2{}^+$ ground state

We consider in some detail the results obtained for the energy as well as for the wave function for the ground state $^2\Sigma_g^+(1s\sigma_g)$ of $H_2{}^+$ at the equilibrium distance $R=2.0$ a.u. We have performed calculations with four basis sets labeled $B1$, $B2$, $B3$, and $B4^*$ which are defined in Table I. For the basis sets $B1$–$B3$ the p values for each TDO have been obtained as described in Sec. II while for the $B4^*$ basis set the values of p have been determined so as to minimize the energy. The exact value reported in Table I corresponds to 36 terms taken into account in Eq. (1) ($k=0,6,2;j=0,9,1$). Values of the electronic energy obtained for each basis set are reported in Table I as well as the relative difference

$$\delta=|\,E(B_i)-E_{\text{exact}}\,|\,/E_{\text{exact}}\ .$$

TABLE I. Basis function and corresponding values (in a.u.) of the electronic energy for the wave functions $1s_{\sigma_g}$ and $2p_{\sigma_u}$ of H_2^+ and $1s_\sigma$ of HeH^{2+} at $R=2.0$ a.u.

	Basis set	J	TDO's n	 l	 m	p	Expansion coefficient c_i	Electronic energy Approximate	 Exact	δ (%)
H_2^+ $1s_{\sigma_g}$	$B1$	1	1	0	0	1.465 895	1	−1.074 424	−1.102 634	2.6
	$B2$	4	1	0	0	1.465 470	−0.999 141	−1.087 990		1.3
			3	2	0	0.488 826	0.036 567			
			5	4	0	0.116 018	0.000 078			
	$B3$	10	1	0	0	1.465 895	0.997 551	−1.100 282		0.2
			2	0	0	0.881 470	−0.019 882			
			3	0	0	0.638 639	−0.004 765			
			4	0	0	0.497 650	−0.015 551			
			5	0	0	0.405 352	−0.000 538			
			3	2	0	0.488 826	0.060 187			
			4	2	0	0.568 070	0.028 534			
			5	2	0	0.497 650	0.005 716			
			6	2	0	0.423 970	0.001 523			
			5	4	0	0.116 018	0.000 096			
	$B4^*$	4	1	0	0	0.779 956	−0.942 678	1.102 536		0.01
			2	0	0	1.054 893	−0.300 198			
			3	0	0	0.844 943	−0.011 443			
			3	2	0	1.382 545	−0.145 286			
H_2^+ $2p_{\sigma_u}$	$B5^*$	5	2	1	0	0.349 990	−0.871 472	−0.667 369	−0.667 534	0.03
			3	1	0	0.461 120	−0.480 757			
			4	1	0	0.613 800	−0.083 888			
			5	1	0	0.728 470	0.022 262			
			4	3	0	0.692 171	−0.043 315			
HeH^{2+} $1s_\sigma$	$B6^*$	4	1	0	0	2.105 292	0.750 277	−2.506 885	−2.512 193	0.2
			2	1	0	2.102 257	−0.593 016			
			3	2	0	2.108 842	0.279 606			
			4	3	0	2.135 845	−0.085 070			

As shown, good accuracy can be achieved with a reduced basis of truncated diatomic orbitals.

To further check the quality of the approximate wave functions

$$\chi=\sum_i c_i \psi_{n_i l_i m_i}(\lambda,\mu,\phi)$$

built up from TDO's ψ, we have computed their values along the molecular axis. The expansion coefficients c_i are reported in Table I. Comparison with exact values is displayed in Table II and Fig. 1(a). A very good agreement is shown for all distances for the wave function corresponding to the basis set $B4^*$.

It is worthwhile to compare our results with the recent single-center ones of Kranz and Steinborn.[26] The main known advantage of single-center expansions of molecular functions as compared with linear combinations of atomic functions (LCAO-MO) is that no multicenter integrals occur in molecular calculations, all the basis functions being centered at a same point. The main disadvantage is that usually many such basis functions are needed for a reasonable accuracy. In fact, for the particular case of diatomic calculations, TDO's expansions would be as easily tractable as are single-center ones. For the ground state of H_2^+ at $R=2.0$ a.u., Kranz and Steinborn centered the expansions at the midpoint of the internuclear axis and they used a set of orthogonal basis function Λ. For a given quality of the energy value obtained, the TDO's basis set is largely more compact than the single-center Λ basis set. For instance, these authors obtained a value of -1.100084 a.u. with a set of 70 Λ functions to be compared to our value of -1.100282 a.u. obtained with a set of ten TDO's ($B3$) (the exact value is -1.102634 a.u.).

The best value they reported is -1.1022 a.u. obtained with a set of 160 Λ functions (one variational parameter) while we obtained -1.102536 a.u. with four TDO's (four variational parameters).

They reproduced very well the exact values of the wave function in the bonding region as well as at large distances with a set of 100 Λ functions while, as expected, they

TABLE II. Values of the wave functions χ $1s_{\sigma_g}$ and $2p_{\sigma_u}$ of H_2^+ and $1s_\sigma$ of HeH^{2+} at $R=2.0$ a.u. along the molecular axis z.

Wave function basis	H_2^+						HeH^{2+}		
		$1s_{\sigma_g}$ [a]			$2p_{\sigma_u}$ [b]			$1s_\sigma$	
z	$B4^*$	Exact	Difference	$B5^*$	Exact	Difference	$B6^*$	Exact	Difference
−2.0				0.198 147	0.198 550	0.000 403	0.185 448	0.193 118	0.007 670
−1.8				0.235 417	0.236 745	0.001 328	0.282 668	0.295 221	0.012 553
−1.6				0.278 803	0.281 023	0.002 220	0.430 857	0.450 490	0.019 633
−1.4				0.329 084	0.331 823	0.002 739	0.656 736	0.685 969	0.029 233
−1.2				0.387 077	0.389 342	0.002 265	1.001 036	1.041 938	0.040 902
−1.0				0.453 619	0.453 348	−0.000 271	1.525 843	1.577 942	0.052 099
−0.8				0.348 294	0.345 928	−0.002 366	1.090 272	1.076 053	−0.014 219
−0.6				0.252 704	0.249 966	−0.002 738	0.760 999	0.740 487	−0.020 512
−0.4				0.164 413	0.162 233	−0.002 180	0.522 343	0.515 646	−0.006 697
−0.2				0.080 990	0.079 813	−0.001 177	0.358 618	0.364 816	0.006 198
0.0	0.314 327	0.314 692	0.000 365	0.0	0.0	0	0.254 144	0.263 753	0.009 609
0.2	0.320 059	0.319 825	−0.000 234				0.193 234	0.196 452	0.003 218
0.4	0.337 253	0.335 507	−0.001 746				0.160 208	0.152 403	−0.007 805
0.6	0.365 910	0.362 611	−0.003 299				0.139 380	0.124 799	−0.014 581
0.8	0.406 030	0.402 654	−0.003 376				0.115 069	0.109 358	−0.005 711
1.0	0.457 613	0.457 896	0.000 283				0.071 590	0.103 605	0.032 015
1.2	0.349 833	0.352 207	0.002 374				0.047 104	0.068 411	0.021 307
1.4	0.267 175	0.270 066	0.002 891				0.030 991	0.045 039	0.014 048
1.6	0.203 844	0.206 542	0.002 698				0.020 388	0.029 578	0.009 190
1.8	0.155 369	0.157 611	0.002 242				0.013 412	0.019 384	0.005 972
2.0	0.118 302	0.120 044	0.001 742				0.008 822	0.012 680	0.003 858

[a] $\chi(z)=\chi(-z)$

[b] $\chi(z)=-\chi(-z)$.

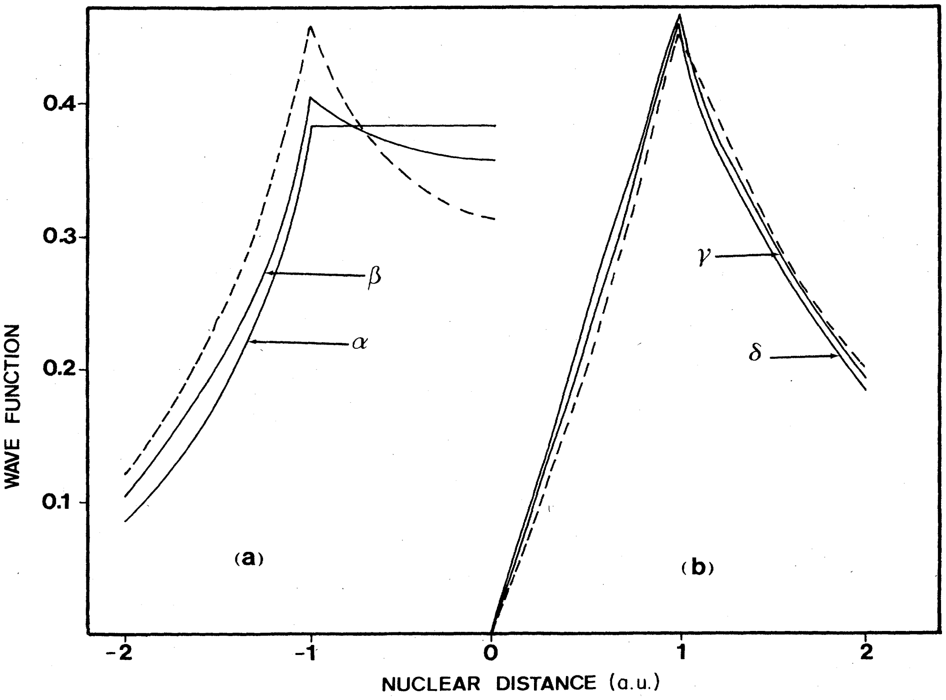

FIG. 1. Normalized wave functions of H_2^+ along the molecular axis for $R=2.0$ a.u. (a) $1s_{\sigma_g}$ (α): basis set $B1$; (β): basis set $B3$; dashed line: basis set $B4^*$ and exact. (b) $2p_{\sigma_u}$ (ν): basis set of three TDO's nonoptimized ($m=0$; $nl=21,31,43$); (δ): basis set of six TDO's nonoptimized ($m=0$; $nl=21,31,41,51,61,43$); dashed line: basis set $B5^*$ and exact. See the text and Table I for the definition of the basis set Bi.

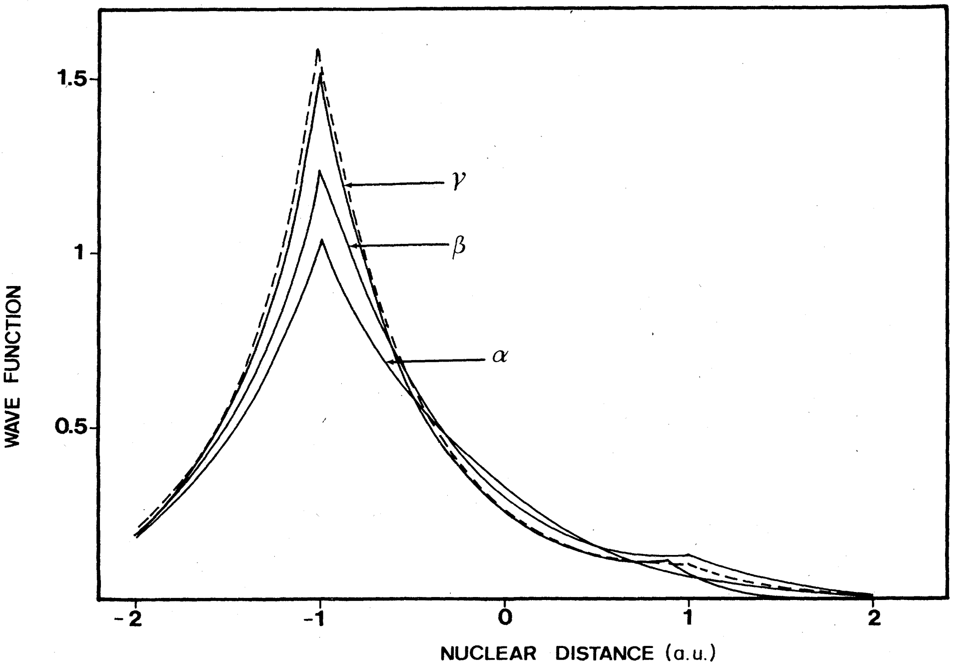

FIG. 2. Normalized wave function $1s_\sigma$ of HeH^{2+} along the molecular axis for $R=2.0$ a.u. (α): basis set of the three TDO's nonoptimized ($m=0$; $nl=10,21,32$); (β): basis set of five TDO's nonoptimized ($m=0$, $nl=10,20,21,31,32$); (ν): basis set $B6^*$ (see the text and Table I); dashed line: exact.

failed in reproducing the cusps of the wave function for values of the distance corresponding to the position of the nuclei. Because of the intrinsic "diatomic" feature of the TDO's we have been able to reproduce with a good accuracy the exact wave functions for all distances.

B. Further results for some molecular states of H_2^+ and HeH^{2+}

We have performed calculations of the electronic energy as well as of the wave function for the state $^2\Sigma_u^+(2p\sigma_u)$ of H_2^+ and for the ground state $1s\sigma$ of HeH^{2+} at $R=2.0$ a.u. The corresponding results are presented and compared with the exact ones in Table I for the energies and in Table II for the wave functions. The basis sets $B5^*$ and $B6^*$ used, respectively, for H_2^+ and HeH^{2+} correspond to optimized values of p. For the $^2\Sigma_u^+(2p\sigma_u)$ state of H_2^+ an excellent agreement is displayed for both the value of the energy and the values of the wave function. For the ground state of HeH^{2+} a good value of the energy and a fairly good description of the wave function are obtained. Values of the wave functions $2p\sigma_u$ of H_2^+ and $1s_\sigma$ of HeH^{2+} are displayed in Figs. 1(b) and 2, respectively, together with the corresponding exact values.

Further test results are presented and compared with the corresponding exact values in Table III for some excited states of H_2^+ and of HeH^{2+}. All these results have been obtained from TDO's with nonoptimized values of p. The relative difference δ as well as the number of TDO's used in the approximate wave functions and the number of terms taken into account in the exact wave functions are quoted.

It should be noted that in all our test calculations, our aim being not to reproduce the known exact values but to illustrate the use of TDO's as basis functions, we have not attempted to make an optimal choice of the various n,l (for a given symmetry m) involved in the different basis sets $B^{(*)}$. Our conclusion from all the whole results obtained is that TDO's are interesting basis functions for the description of one-electron diatomic systems.

IV. TDO'S AS BASIS FUNCTIONS FOR THE DESCRIPTION OF MOLECULAR STATES OF Li_2^+

After having ascertained that TDO's may be advantageously used to describe true one-electron diatomic sys-

TABLE III. Values of the electronic energy (in a.u.) for some excited states of H_2^+ and HeH^{2+}.

			Energy		Relative difference δ	Number of	Number of terms in the
		State	Approximate	Exact	(%)	TDO's	exact solution
H_2^+	$m=0$	$2s_{\sigma_g}$	−0.390 25	−0.394 88	1.2	13	40
	$R=1.4$	$3d_{\sigma_g}$	−0.227 98	−0.228 30	0.15	18	30
		$2p_{\sigma_u}$	−0.608 74	−0.612 08	0.5	15	30
		$3p_{\sigma_u}$	−0.246 68	−0.248 64	0.8	14	30
	$m=1$	$2p_{\Pi_u}$	−0.449 92	−0.451 73	0.4	14	30
	$R=1.5$	$3p_{\Pi_u}$	−0.205 75	−0.207 87	1.0	14	36
		$4f_{\Pi_u}$	−0.125 65	−0.125 67	0.02	13	48
		$3d_{\Pi_g}$	−0.225 00	−0.225 01	0.005	8	30
		$4d_{\Pi_g}$	−0.126 02	−0.126 12	0.07	9	48
		$5d_{\Pi_g}$	−0.080 34	−0.080 55	0.25	10	40
	$m=2$	$3d_{\delta_g}$	−0.216 25	−0.216 51	0.12	11	36
	$R=1.5$	$4d_{\delta_g}$	−0.122 39	−0.122 60	0.15	11	36
		$5g_{\delta_g}$	−0.080 08	−0.080 08	0.001	13	36
		$4f_{\delta_u}$	−0.124 95	−0.124 99	0.03	14	36
		$5f_{\delta_u}$	−0.079 93	−0.079 99	0.08	14	27
		$6h_{\delta_u}$	−0.055 57	−0.055 59	0.04	15	36
HeH^{2+}	$m=0$	$2p_\sigma$	−1.339 07	−1.345 18	0.6	25	60
	$R=2$	$2s_\sigma$	−0.785 29	−0.787 09	0.2	22	72
		$3d_\sigma$	−0.571 11	−0.571 25	0.02	25	54
		$3p_\sigma$	−0.532 62	−0.536 63	0.4	21	88
	$m=1$	$2p_\Pi$	−0.898 18	−0.899 65	0.2	19	40
	$R=2$	$3d_\Pi$	−0.512 38	−0.512 61	0.05	20	60
		$3p_\Pi$	−0.428 91	−0.431 23	0.5	19	96
	$m=2$	$3d_\delta$	−0.462 92	−0.463 29	0.08	14	84
	$R=2$	$4f_\delta$	−0.280 69	−0.280 81	0.05	15	80

TABLE IV. Values of the electronic energy for various values of the internuclear distance (in a.u.) for some molecular states $^2\Sigma_g^+$ of Li$_2$.

State R	$X^2\Sigma_g^+$	$2^2\Sigma_g^+$	$3^2\Sigma_g^+$	$4^2\Sigma_g^+$	$5^2\Sigma_g^+$	$6^2\Sigma_g^+$	$7^2\Sigma_g^+$	$8^2\Sigma_g^+$	$9^2\Sigma_g^+$
2	−0.474 14	−0.271 94	−0.209 83	−0.149 78	−0.119 21	−0.093 14	−0.080 37	−0.076 90	−0.063 22
3	−0.468 30	−0.316 87	−0.200 22	−0.162 62	−0.114 41	−0.098 45	−0.080 85	−0.074 25	−0.065 94
4	−0.465 14	−0.305 54	−0.196 66	−0.155 90	−0.112 41	−0.094 95	−0.081 56	−0.073 08	−0.063 93
5	−0.441 52	−0.288 03	−0.192 24	−0.147 71	−0.110 36	−0.090 77	−0.082 51	−0.071 95	−0.061 55
6	−0.412 34	−0.273 25	−0.186 70	−0.140 56	−0.108 11	−0.087 03	−0.083 78	−0.070 76	−0.059 39
7	−0.348 30	−0.261 49	−0.180 53	−0.134 59	−0.105 78	−0.085 50	−0.083 82	−0.069 62	−0.058 88
8	−0.359 45	−0.252 02	−0.174 17	−0.129 70	−0.103 61	−0.087 85	−0.081 10	−0.068 69	−0.060 49
9	−0.338 13	−0.244 10	−0.167 96	−0.125 77	−0.102 06	−0.090 87	−0.078 87	−0.068 47	−0.062 20
10	−0.320 17	−0.237 14	−0.162 16	−0.122 84	−0.102 63	−0.093 20	−0.077 28	−0.069 68	−0.063 00
11	−0.305 25	−0.230 70	−0.156 97	−0.121 27	−0.105 99	−0.092 93	−0.076 76	−0.070 86	−0.062 57
12	−0.292 99	−0.224 53	−0.152 58	−0.121 63	−0.108 47	−0.091 41	−0.077 31	−0.079 60	−0.061 71
13	−0.283 02	−0.218 48	−0.149 19	−0.123 15	−0.108 60	−0.089 68	−0.077 96	−0.069 63	−0.060 76
14	−0.274 91	−0.212 56	−0.146 88	−0.123 93	−0.107 57	−0.088 04	−0.078 24	−0.068 52	−0.059 82
15	−0.268 31	−0.206 84	−0.145 44	−0.123 34	−0.106 18	−0.086 62	−0.078 07	−0.067 44	−0.058 93
16	−0.262 87	−0.201 43	−0.144 39	−0.121 72	−0.104 73	−0.085 46	−0.077 48	−0.066 43	−0.058 15
18	−0.254 42	−0.191 83	−0.141 99	−0.117 22	−0.101 83	−0.083 74	−0.075 42	−0.064 64	−0.056 84
20	−0.248 10	−0.184 10	−0.138 37	−0.112 70	−0.099 00	−0.082 34	−0.072 90	−0.063 12	−0.055 84

tems we use them for the description of molecular states of Li$_2{}^+$ considered as a diatomic system with one valence electron.

A. The Li$_2{}^+$ problem

In the framework of a model-potential method, the equation for the movement of one electron in the field of two identical alkali-metal Li$^+$ (noted A and B) may be written as follows:

$$[-\tfrac{1}{2}\Delta+\mathscr{V}(\mathbf{r}_A+\mathbf{r}_B;\mathbf{R})-\epsilon(R)]\phi(\mathbf{r}_A,\mathbf{r}_B;\mathbf{R})=0\;, \tag{6}$$

where $\mathscr{V}$ is a molecular model potential defined as:

$$\mathscr{V}(\mathbf{r}_A,\mathbf{r}_B;\mathbf{R})=V(r_A)+V(r_B)+V_{\text{pol}}(\mathbf{r}_A,\mathbf{r}_B;\mathbf{R})+V_{\text{c-c}}(R)\;. \tag{7}$$

For the interaction terms $V(r)$ describing the interaction between the ionic core Li$^+$ and the valence electron we have chosen the parametric form proposed by Klapisch[27]

$$V(r)=-\frac{1+(Z-1)e^{-\alpha_1 r}+\alpha_2 r e^{-\alpha_3 r}}{r}\;, \tag{8}$$

where α_1, α_2, and α_3 are variational parameters determined by this author in order to reproduce the atomic energy spectrum. A very good agreement is displayed for Li

TABLE V. Values of the electronic energy for various values of the internuclear distance (in a.u.) for some molecular states $^2\Sigma_u^+$ of Li$_2{}^+$.

State R	$1^2\Sigma_u^+$	$2^2\Sigma_u^+$	$3^2\Sigma_u^+$	$4^2\Sigma_u^+$	$5^2\Sigma_u^+$	$6^2\Sigma_u^+$	$7^2\Sigma_u^+$	$8^2\Sigma_u^+$	$9^2\Sigma_u^+$
2	−0.360 28	−0.172 88	−0.126 75	−0.102 48	−0.080 93	−0.067 94	−0.056 11	−0.055 67	−0.048 37
3	−0.339 61	−0.164 26	−0.129 30	−0.098 21	−0.082 35	−0.065 54	−0.056 96	−0.055 82	−0.046 90
4	−0.323 32	−0.158 01	−0.133 88	−0.095 30	−0.085 00	−0.063 97	−0.058 58	−0.056 03	−0.045 96
5	−0.311 82	−0.158 41	−0.139 73	−0.097 48	−0.087 26	−0.065 78	−0.059 55	−0.056 30	−0.047 26
6	−0.304 17	−0.172 29	−0.139 97	−0.104 68	−0.086 11	−0.069 51	−0.058 63	−0.056 64	−0.049 41
7	−0.299 02	−0.187 52	−0.137 47	−0.108 92	−0.084 35	−0.071 21	−0.057 52	−0.057 05	−0.050 25
8	−0.294 93	−0.196 65	−0.134 97	−0.110 30	−0.082 79	−0.071 52	−0.057 55	−0.056 55	−0.050 32
9	−0.290 91	−0.200 62	−0.132 80	−0.110 16	−0.081 48	−0.071 12	−0.058 15	−0.055 73	−0.049 99
10	−0.286 61	−0.201 49	−0.130 89	−0.109 22	−0.080 36	−0.070 36	−0.058 86	−0.055 05	−0.049 45
11	−0.282 04	−0.200 69	−0.129 15	−0.107 88	−0.079 40	−0.069 41	−0.059 71	−0.054 47	−0.048 81
12	−0.277 38	−0.199 00	−0.127 50	−0.106 35	−0.078 54	−0.068 39	−0.060 74	−0.053 98	−0.048 12
13	−0.272 78	−0.196 84	−0.125 91	−0.104 77	−0.077 81	−0.067 35	−0.062 02	−0.053 60	−0.047 43
14	−0.268 37	−0.194 47	−0.124 36	−0.103 19	−0.077 23	−0.066 33	−0.063 61	−0.053 39	−0.046 75
15	−0.264 21	−0.191 99	−0.122 86	−0.101 66	−0.076 91	−0.065 51	−0.065 34	−0.053 46	−0.047 47
16	−0.260 35	−0.189 51	−0.121 43	−0.100 20	−0.077 10	−0.067 49	−0.064 41	−0.053 96	−0.048 39
17	−0.256 79	−0.187 05	−0.120 06	−0.098 81	−0.078 13	−0.068 99	−0.063 53	−0.054 81	−0.048 78
18	−0.253 51	−0.184 65	−0.118 77	−0.097 48	−0.080 02	−0.069 65	−0.062 72	−0.055 72	−0.048 77
19	−0.250 52	−0.182 34	−0.177 56	−0.096 24	−0.082 26	−0.069 68	−0.061 96	−0.056 47	−0.048 57
20	−0.247 77	−0.180 12	−0.116 42	−0.095 06	−0.084 37	−0.069 39	−0.061 29	−0.057 02	−0.048 28

TABLE VI. Values of the electronic energy for various values of the internuclear distance (in a.u.) for some molecular states $^2\Pi_{g/u}$ of $\mathrm{Li_2}^+$.

State R	$1^2\Pi_u$	$1^2\Pi_g$	$2^2\Pi_u$	$3^2\Pi_u$	$2^2\Pi_g$	$3^2\Pi_g$	$4^2\Pi_u$	$4^2\Pi_g$	$5^2\Pi_u$	$5^2\Pi_g$
2	−0.468 97	−0.226 52	−0.213 48	−0.126 30	−0.126 60	−0.080 78	−0.121 35	−0.080 32	−0.078 39	−0.055 73
3	−0.407 20	−0.230 67	−0.194 37	−0.127 95	−0.127 92	−0.081 36	−0.113 12	−0.080 72	−0.080 28	−0.056 15
4	−0.363 66	−0.232 87	−0.179 94	−0.130 31	−0.128 05	−0.081 35	−0.106 71	−0.081 19	−0.082 12	−0.056 32
5	−0.330 39	−0.232 55	−0.168 29	−0.133 26	−0.127 00	−0.082 07	−0.101 40	−0.080 53	−0.083 92	−0.056 76
6	−0.303 94	−0.230 19	−0.158 57	−0.136 43	−0.125 16	−0.083 03	−0.096 86	−0.079 43	−0.085 52	−0.057 32
7	−0.282 41	−0.226 52	−0.150 37	−0.139 29	−0.122 89	−0.084 21	−0.092 93	−0.078 11	−0.086 71	−0.057 99
8	−0.264 61	−0.222 14	−0.144 35	−0.140 48	−0.120 43	−0.085 60	−0.089 66	−0.076 61	−0.087 22	−0.058 79
9	−0.249 73	−0.217 45	−0.014 09	−0.135 93	−0.117 91	−0.087 19	−0.088 36	−0.075 28	−0.085 68	−0.059 66
10	−0.237 22	−0.212 71	−0.144 53	−0.130 50	−0.115 42	−0.088 92	−0.088 13	−0.073 87	−0.083 01	−0.060 56
11	−0.226 67	−0.208 10	−0.144 23	−0.125 56	−0.113 00	−0.090 70	−0.087 73	−0.072 50	−0.080 45	−0.061 43
12	−0.217 74	−0.203 69	−0.143 18	−0.121 11	−0.110 69	−0.092 45	−0.087 11	−0.071 17	−0.078 08	−0.062 20
13	−0.210 17	−0.199 54	−0.141 51	−0.117 11	−0.108 49	−0.094 05	−0.086 33	−0.069 91	−0.075 91	−0.062 84
14	−0.203 74	−0.195 68	−0.139 34	−0.113 50	−0.106 43	−0.095 42	−0.085 41	−0.068 71	−0.073 90	−0.063 33
15	−0.198 26	−0.192 10	−0.136 80	−0.110 25	−0.104 50	−0.096 49	−0.084 38	−0.067 57	−0.072 05	−0.063 65
16	−0.193 56	−0.188 79	−0.134 00	−0.107 31	−0.102 75	−0.097 23	−0.083 27	−0.066 52	−0.070 34	−0.062 81
17	−0.189 50	−0.185 76	−0.131 05	−0.104 66	−0.101 24	−0.097 55	−0.082 09	−0.065 59	−0.068 75	−0.063 78
18	−0.185 96	−0.182 97	−0.128 02	−0.102 25	−0.100 15	−0.097 30	−0.080 87	−0.064 87	−0.067 29	−0.063 48
19	−0.182 86	−0.180 41	−0.124 98	−0.100 08	−0.099 53	−0.096 43	−0.079 62	−0.064 41	−0.066 85	−0.062 87
20	−0.180 11	−0.178 06	−0.121 97	−0.098 10	−0.099 11	−0.095 25	−0.078 34	−0.064 09	−0.067 79	−0.062 10

TABLE VII. Values of the electronic energy for various values of the internuclear distance (in a.u.) for some molecular states $^2\Delta_{g/u}$ of $\mathrm{Li_2}^+$.

State R	$1^2\Delta_g$	$1^2\Delta_u$	$2^2\Delta_g$	$3^2\Delta_g$	$2^2\Delta_u$	$4^2\Delta_g$	$3^2\Delta_u$	$5^2\Delta_g$	$4^2\Delta_u$	$5^2\Delta_u$
2	−0.216 10	−0.124 96	−0.123 00	−0.080 14	−0.079 98	−0.079 11	−0.055 61	−0.054 36	−0.055 05	−0.039 30
3	−0.206 40	−0.124 83	−0.118 89	−0.080 32	−0.079 89	−0.077 00	−0.055 71	−0.054 87	−0.055 17	−0.039 74
4	−0.196 66	−0.124 52	−0.114 67	−0.080 56	−0.079 68	−0.074 82	−0.055 83	−0.055 30	−0.055 14	−0.040 11
5	−0.187 05	−0.123 95	−0.110 50	−0.080 85	−0.079 31	−0.072 67	−0.055 98	−0.055 65	−0.054 97	−0.040 44
6	−0.178 02	−0.123 11	−0.106 54	−0.081 17	−0.078 78	−0.070 59	−0.056 17	−0.055 95	−0.054 68	−0.040 73
7	−0.169 66	−0.122 02	−0.102 80	−0.081 51	−0.078 11	−0.068 61	−0.056 39	−0.056 20	−0.054 28	−0.040 99
8	−0.161 98	−0.120 70	−0.099 28	−0.081 83	−0.077 31	−0.066 74	−0.056 64	−0.056 40	−0.053 81	−0.041 24
9	−0.154 95	−0.119 19	−0.096 11	−0.082 13	−0.076 43	−0.064 97	−0.056 92	−0.056 55	−0.053 27	−0.041 48
10	−0.148 53	−0.117 56	−0.092 95	−0.082 36	−0.075 47	−0.063 31	−0.057 22	−0.056 44	−0.052 69	−0.041 71
11	−0.142 65	−0.015 83	−0.090 10	−0.082 53	−0.074 47	−0.061 74	−0.057 54	−0.056 67	−0.052 08	−0.041 93
12	−0.137 27	−0.114 04	−0.087 44	−0.082 61	−0.073 45	−0.060 25	−0.057 88	−0.056 64	−0.051 46	−0.042 14
13	−0.132 33	−0.112 23	−0.084 95	−0.082 59	−0.072 42	−0.058 86	−0.058 22	−0.056 55	−0.050 83	−0.042 35
14	−0.127 80	−0.110 42	−0.082 71	−0.082 39	−0.071 38	−0.057 54	−0.058 56	−0.056 40	−0.050 19	−0.042 53
15	−0.123 63	−0.108 62	−0.082 29	−0.080 43	−0.070 36	−0.056 37	−0.058 89	−0.056 13	−0.049 56	−0.042 70
16	−0.119 80	−0.106 86	−0.081 99	−0.078 39	−0.069 35	−0.056 00	−0.059 21	−0.055 08	−0.048 94	−0.042 85
17	−0.116 26	−0.105 14	−0.081 60	−0.076 47	−0.068 36	−0.055 71	−0.059 50	−0.053 91	−0.048 33	−0.042 98
18	−0.112 99	−0.103 46	−0.081 12	−0.074 66	−0.067 39	−0.055 39	−0.059 76	−0.052 90	−0.047 73	−0.043 08
19	−0.109 98	−0.101 84	−0.080 57	−0.072 97	−0.066 45	−0.055 05	−0.059 99	−0.051 88	−0.047 14	−0.043 16
20	−0.107 21	−0.100 28	−0.079 95	−0.071 37	−0.065 53	−0.054 68	−0.060 17	−0.050 92	−0.046 57	−0.043 21

between calculated and experimental energy spectrum for the following values of the parameters:

$$\alpha_1=7.9,\quad \alpha_2=10.31,\quad \alpha_3=3.898\ .$$

V_{pol} represents the whole polarization effects, i.e., each ionic core Li^+ is polarized by the simultaneous electric field due to the valence electron and due to the other Li^+ core. This whole effect appears as a sum of the three

TABLE VIII. Comparative results for the spectroscopic constants R_e and D_e of some molecular states of $\text{Li}_2{}^+$.

Molecular state	Method	R_e (Å)	D_e (eV)
$X\,^2\Sigma_g^+$	Model potential[a,b,c]	3.1	1.31
		3.08	1.30
		3.09	1.28
	Pseudopotential[d]	3.09	1.30
	Frozen-core[e]	3.16	1.26
	SCF^{+}	3.127	1.280
	SCF + core polarization potential[g]	3.099	1.293
	Valence configuration + effective core potential (ECP)[h]	3.076	1.314
	Present work	3.08	1.30
	Experimental[i,j,k]	3.11±0.01	1.27±0.02
			1.2980±0.0007
			1.2836±0.0031
$2\,^2\Sigma_g^+$	SCF[l]	6.88	0.299
	Model potential[a]	6.77	0.30
	Frozen-core[e]	6.88	0.31
	Valence configuration + ECP[h]	6.84	0.309
	Present work	6.85	0.31
$1\,^2\Sigma_u^+$	SCF[f]	10.3	0.01
	Model potential[a]	10	0.01
	Frozen-core[e]	10.0	0.01
	Valence configuration + ECP[h]	9.92	0.01
	Present work	9.24	0.01
$1\,^2\Pi_u$	SCF[f]	4.01	0.23
	Model potential[a]	4.02	0.23
	Frozen-core[e]	4.02	0.25
	Valence configuration + ECP[h]	3.987	0.236
	Present work	3.97	0.26
$2\,^2\Pi_u$	Frozen-core[e]	10.32	0.37
	Present work	9.59	0.41
$1\,^2\Delta_g$	Frozen-core[e]	9.53	0.035
	Present work	9.28	0.05

[a] Reference 31.
[b] Reference 39 when neglecting V_3 (see the text).
[c] Reference 39 when including V_3.
[d] Reference 4.
[e] Reference 35.
[f] Reference 36.
[g] Reference 38.
[h] Reference 41.
[i] Reference 42.
[j] Reference 43.
[k] Reference 44.
[l] Reference 37.

terms: a valence electron-core polarization term, a core-core polarization term, and a cross term due to the nonadditivity of the various polarization contributions. Mathematical forms generally used to take these effects into account are derived from the asymptotic form of the molecular potential given by Bottcher and Dalgarno,[28] multiplied by a convenient cutoff function in order to avoid divergence at small values of the distance. As a first step, we have neglected all these polarization effects in our present calculations on Li_2^+ arguing that Li is a light atom with not much of a polarizable core.

$V_{\text{c-c}}$ represents the core-core interaction apart from the polarization terms already considered in V_{pol}. For values of R such that the overlap between the core wave functions is small, the interactions between the two Li^+ is largely dominated by the long-range charge-charge term $1/R$. For smaller values of R, exchange effects are to be taken into account. Such short-range interactions have been included either in an empirical way[29] or in a theoretical one.[30] In our present calculations $V_{\text{c-c}}$ has been restricted to the predominant term $1/R$.

B. Calculations and results

The molecular potential $\mathscr{V}$ [Eq. (7)] being defined for Li_2^+, we solved Eq. (6) written in prolate-spheroidal coordinates on the basis of TDO's. The values of p for each basis function ψ_{nlm} are derived from Eq. (5) with $Z_A = Z_B = 3$.

We have paid particular attention to the choice of the various n,l in building up the basis sets for a given symmetry m. After some systematic investigations we have adopted the following automatic procedure.

(i) First we add TDO's with increasing l values (by a step of 2 for homonuclear cases) until the numerical values of the eigenenergies of interest are stabilized (to a chosen precision).

(ii) Then for each l value (starting from the smallest) we add TDO's with increasing n values until the numerical stabilization of the eigenvalues of interest.

Calculations have been performed for the nine lowest-lying states of symmetry Σ_g and of symmetry Σ_u, the five lowest-lying states of symmetry Π_g, and of symmetry Π_u, the five lowest-lying states of symmetry Δ_g and of symmetry Δ_u, in the range $2.0 \leq R \leq 20$ a.u. of internuclear distances. Results for the electronic energy are presented in Table IV for the ${}^2\Sigma_g^+$ states, in Table V for the ${}^2\Sigma_u^+$ states, in Table VI for the ${}^2\Pi_{g,u}$ states, and in Table VII for the ${}^2\Delta_{g,u}$ states. The number of TDO's used for states of a given symmetry are also quoted. Some comparative results about the quantities R_e and D_e (in Å and eV, respectively, for ease of comparison) are gathered in Table VIII.

Several theoretical investigations of the ground state $X^2\Sigma_g^+$ of Li_2^+ have been performed recently[31–41,4] including model potential, pseudopotential, and *ab initio* calculations. As shown in Table VIII our determinations for R_e and D_e are in good agreement with recent literature ones. We pay some further attention to the comparison between our results and the very recent ones reported by Henriet and Masnou-Seeuws[39] for a lot of $\Sigma_{g,u}$ states of Li_2^+. These authors included core-core polarization effects (i.e., $-\alpha_{Li^+}/R^4$ where α_{Li^+} is the static dipolar polarizability of the core Li^+) in the molecular potential $\mathscr{V}$ [Eq. (7)] for any value of R and they performed two types of calculations: one in taking into account the cross polarization term (noted V_3 in their paper), the other in neglecting it. As we have done, they represented the valence electron-core interactions through the Klapisch potential. They solved the Li_2^+ problem with a set of 134 prolate-spheroidal generalized Slater functions. Then, our present values for the total energy corrected by the core-core polarization term

$$E_T(R) = \epsilon(R) - \alpha_{Li^+}/R^4$$

are directly comparable to their results corresponding to $V_3 = 0$. As a matter of fact, when comparing the two sets of results for various values of R,[40] it appears that they are in very good agreement. It should be noted that the correction due to the cross polarization term V_3 is seen to be small for Li_2^+ and it decreases with increasing values of R.[40]

A good agreement with the literature results including *ab initio*,[36,37,41] model potential,[21] and frozen-core method ones[35] is displayed for R_e and D_e of the first excited $2^2\Sigma_g^+$ state as well as for the dissociation energy of the first excited $1^2\Sigma_u^+$ state, while our value for R_e is smaller by an amount of roughly 10%.

For the first excited state ${}^2\Pi_u$ present values of R_e and D_e are in reasonable agreement with previous determinations.[31,35–36,41] For the states $2^2\Pi_u$ and $1^2\Delta_g$ we compare our results with the corresponding frozen-core method

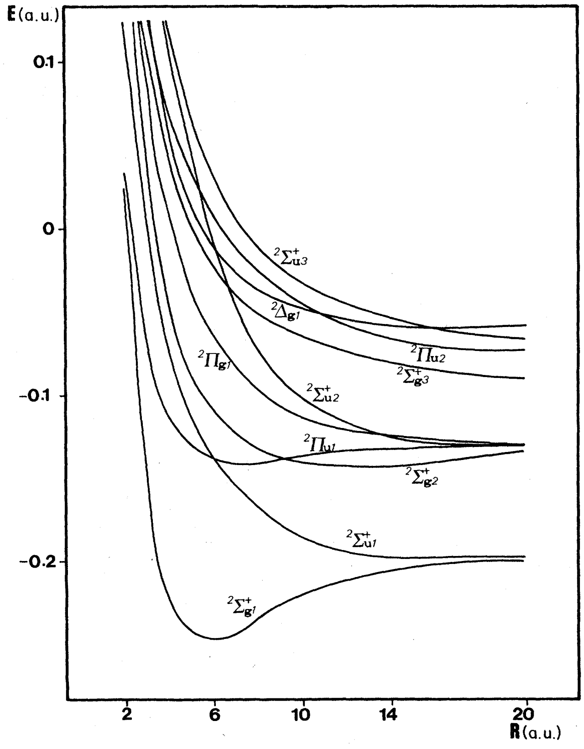

FIG. 3. Potential energy curves for the ten lowest-lying states of Li_2^+.

ones given by Müller and Jungen:[35] They are in fairly good agreement for R_e while present values are significantly larger than previous ones for D_e.

For the remaining states a direct comparison may be made for nuclear separations between 2 and 20 a.u. with the tables of results given by Müller and Jungen for a large number of states: six $^2\Sigma_g^+$ states, five $^2\Sigma_u^+$ states, five $^2\Pi_u$ states, four $^2\Pi_g$ states, four $^2\Delta_g$ states, and three $^2\Delta_u$ states. Our conclusion is that the two sets of results are in fairly good agreement. The curves for the total energy of the ten lowest-lying molecular states of $Li_2{}^+$ are drawn in Fig. 3.

V. CONCLUSION

We have defined truncated diatomic orbitals (TDO's) in retaining only one term in the expansions of the eigenfunctions (in prolate-spheroidal coordinates) of one-electron diatomic systems and we have presented a simple procedure to determine the parameter involved in their mathematical form. Test calculations for some exactly known molecular states of $H_2{}^+$ and HeH^{2+} have shown that compact basis sets of TDO's provide good approximations of the exact values of the eigenenergies as well as of the exact values of the wave functions.

We have then described 38 electronic states of $Li_2{}^+$ in the framework of a model potential method, using TDO's as basis functions. Again, compact basis sets are sufficient to achieve a good accuracy. Preliminary results of a similar work now in progress for LiH^+, $Na_2{}^+$, and NHe^{6+} corroborate this result. The number of basis functions needed to approximate wave functions of effective one-electron diatomic systems is a very sensitive criterion for us because we have undertaken to use these approximate functions in Pluvinage's method[9] to determine explicitly correlated functions as well as in usual configuration interaction approach to describe molecular states of effective two-electron diatomic species.

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